[AMERICAN JOURNAL OF SCIENCE, VOL. 278, OCTOBER, 1978, P. 1177-1184]

DOLOMITIZATION IN THE FLORIDAN AQUIFER*

ANTHONY F. RANDAZZO and EDWIN W. HICKEY

Department of Geology, University of Florida,
Gainesville, Florida 32611

ABSTRACT. Multiple transgressive-regressive cycles of sedimentation characterize 20 cores penetrating the Floridan Aquifer. Original texture is preserved more frequently in rocks deposited in a supratidal environment and replaced by stoichiometric dolomite. Non-stoichiometric dolomite commonly is associated with obscured or obliterated limestone fabrics.

Strontium in both dolomite groups generally is less than 250 ppm and indicates crystallization in a solution less saline than seawater. Dolomitization continued with time as rocks of supratidal and other environments of the area were subjected to repeated lateral migrations of a saltwater-freshwater interface and phreatic groundwaters.

INTRODUCTION

The Avon Park and Ocala Limestones (Middle and Upper Eocene respectively) are the principal units composing the Floridan Aquifer. Analysis of 20 cores penetrating these formations in northwestern peninsular Florida (fig. 1) has established lithofacies representing multiple transgressive-regressive cycles of sedimentation. Petrographic examination has revealed microfacies characteristic of paleoenvironments such as shallow shelf, subtidal, intertidal, and supratidal (Randazzo and Saroop, 1976). The effects of marine transgressions and regressions, water energy levels, and geomorphic positions have been recognized.

Petrographic controls significant to the functioning of hydrologic systems have been identified and described (Randazzo, Stone, and Saroop, 1977). Such controls are a manifestation of the type, condition, and abundance of the allochemical and orthochemical constituents of the various carbonate rocks. Attention to these constituents has brought to light the diagenetic changes that have occurred since burial.

Randazzo, Stone, and Saroop (1977) described several textures of dolomitization, the most important of which were: (1) dolomitization by total replacement with preservation of original fabric (pl. 1-A), and (2) dolomitization involving aggrading porphyroid and coalescive neomorphism (pl. 1-B). The total-replacement dolomites were associated more closely with supratidal sediments and evaporite minerals, whereas the neomorphic textures could be found in rocks originally deposited in the supratidal, intertidal, shallow and deep subtidal environments, in other words, all that were recognized.

DOLOMITE

In this study dolomite is categorized chemically by its $MgCO_3$ content. Mol-percent $MgCO_3$ was determined by X-ray diffraction, utilizing computer corrections for d-spacing and lattice parameter refinement and the curves of Goldsmith and Graf (1958b). Specific methodologies used are stated in Hickey (ms). Because of the limitations of the analytical

---

* Paper presented at the Second International Symposium on Water-Rock Interaction, Strasbourg, France, 1977.

procedures and instrumentation, data were rounded off to the nearest whole percent. Stoichiometric dolomite contains 49 to 51 mol-percent $MgCO_3$. Non-stoichiometric dolomite is composed of 44 to 48 mol-percent $MgCO_3$ and is similar to the non-ideal dolomite referred to by Goldsmith and Graf (1958a). These dolomite categories are found among all the textural types of Randazzo and Saroop (1976).

Stoichiometric dolomite crystals are usually sub- to euhedral, equant, rhombohedrons in the 10 to 30 μ size-range. Crystals commonly are zoned with opaque centers of an indeterminate origin and clear rims or display dissolved centers. Where original fabrics have been preserved, dolomitized rocks generally are foraminiferal packstones, wackestones, and mudstones (Dunham, 1962). Delicate foraminiferal structures commonly are well-preserved. Occurring with stoichiometric dolomite are prismatic molds of gypsum crystals as large as 2 × 0.05 mm (pl. 2-A). The molds are similar in shape to crystals of gypsum found in modern evaporative supratidal environments, where they are associated with comparable lithologies (Illing, Wells, and Taylor, 1965; Summerson, 1966; Kinsman, 1969a). The euhedral gypsum crystals displaced unlithified carbonate sediments as they grew, causing a disruption of carbonate laminae.

Non-stoichiometric crystals of dolomite are subhedral or euhedral rhombohedrons, 10 to 80 μ in size, and usually contain opaque, central inclusions of an indeterminate origin. Their slightly larger size and their association most often with obscured or obliterated original depositional textures are the principal microscopic differences from stoichiometric dolomite.

Representative samples were chosen from each gross lithology found in three cores for strontium analyses by means of Atomic Absorption Spectrometry. In order to detect any additional distinctions between the two dolomite groups only rocks shown to be 100 percent dolomite were used, because, supposedly, calcite contains approximately twice the strontium substitution sites as dolomite (Behrens and Land, 1972). A plot of strontium content versus mol-percent $MgCO_3$ (fig. 2) shows two dis-

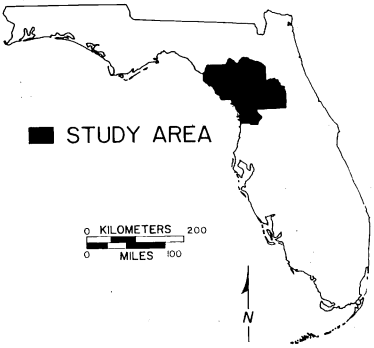
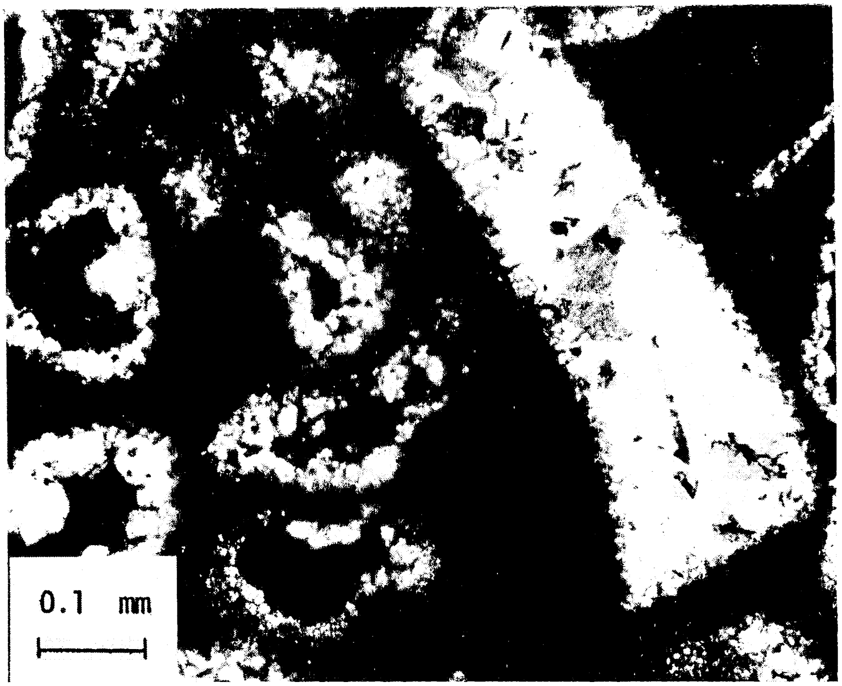
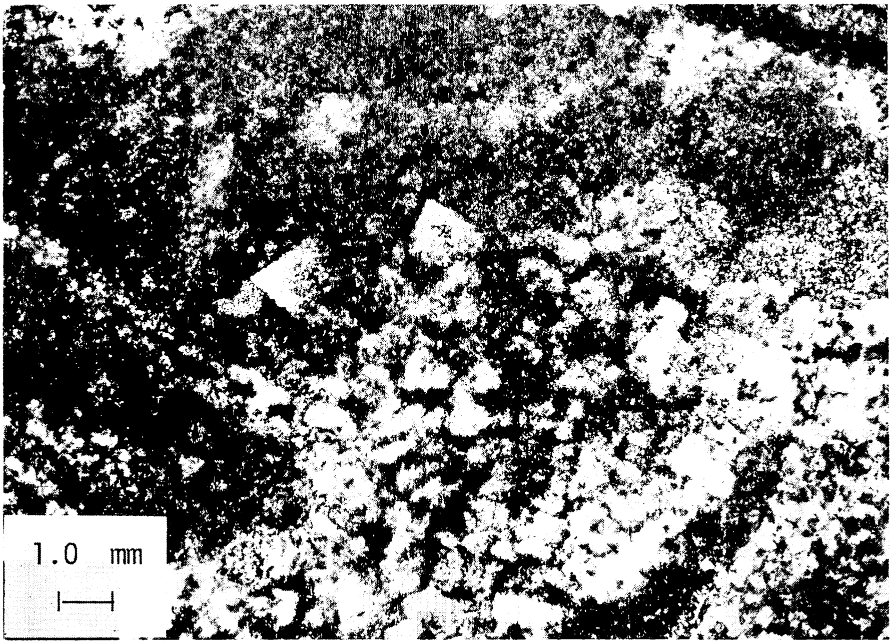


Fig. 1. Location map of the study area.

PLATE 1



A. Dolomitization by total replacement. The recognizable foraminiferal tests and pelecypodal valves represent the high degree of preservation of the original texture of this sample despite complete replacement by dolomite (X-nicols).



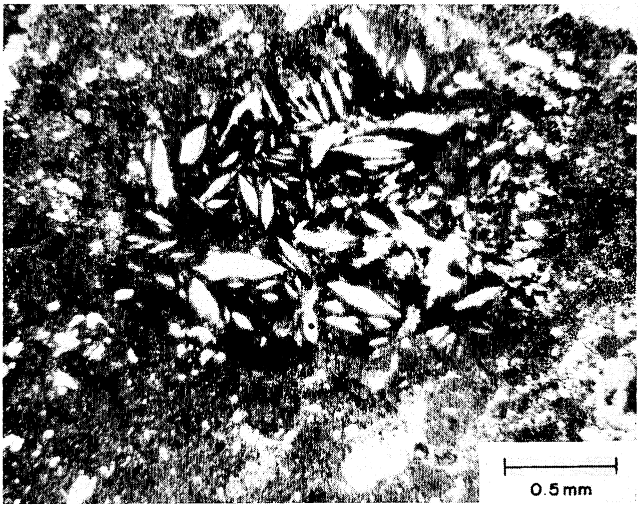
B. Dolomitization through porphyroid neomorphism. This sample shows the process at a very early stage of development, where only a few, incompletely formed, dolomite-rhombs are present in a groundmass of calcite (X-nicols).

tinct groups — a lower strontium-higher mol-percent $MgCO_3$ (stoichiometric dolomite) and a higher strontium-lower mol-percent $MgCO_3$ (non-stoichiometric dolomite). A student t paired different test supports the separation of the strontium-mol-percent $MgCO_3$ groups at the 99 percent confidence level. Data are summarized in table 1.

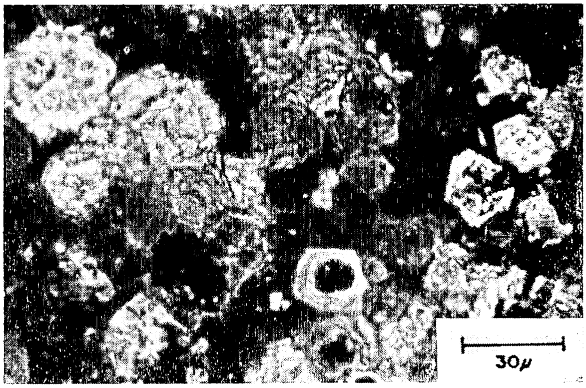
DISCUSSION

Penecontemporaneous dolomite, occurring in modern environments, generally forms in thin crusts at or near the surface. The dolomite is non-stoichiometric, ranges in crystal size from 1 to 5 μ, and has a relatively high content of strontium (Veizer and Demovíc, 1974). Hypersaline brines, associated with evaporite conditions, commonly are the dolomitizing fluids in the supratidal zone (Illing, Wells, and Taylor,

PLATE 2



A. Prismatic crystal molds of gypsum in a groundmass of stoichiometric dolomite.



B. Crystals of dolomite with hollow centers.

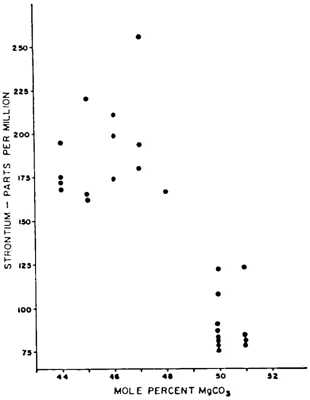


Fig. 2. Plot of strontium content versus mol-percent $MgCO_3$.

1965; Shinn, Ginsburg, and Lloyd, 1965). Dolomitization has been shown to occur also in the zone of mixing of phreatic and meteoric waters with seawater (Land, Salem, and Morrow, 1975) or from a dilute saline solution within a phreatic groundwater system (Hanshaw, Back, and Deike, 1971). Randazzo, Stone, and Saroop (1977) reported that the type and distribution of the textures of dolomite indicated an early stage of dolomitization associated with a supratidal environment and a later and continuing stage associated with migration of a saltwater-freshwater interface.

Folk, Roberts, and Moore (1973) and Folk and Land (1975) suggest that stoichiometric dolomite precipitates as euhedral limpid crystals of dolomite, ranging from 20 to 100 μ in size, slowly from dilute saline or freshwater solutions. Relatively low strontium-content in dolomite reflects a relatively low salinity of the last recrystallizing fluid (Kinsman, 1969b; Behrens and Land, 1972; Land, Salem, and Morrow, 1975; Al-Hashimi, 1976).

All the dolomites analyzed contain significantly less strontium than expected in dolomite in equilibrium with a solution of a normal marine salinity and are comparable to dolomites that have undergone neomorphism in solutions of dilute saline or freshwater (table 2). The dolomite either crystallized in a solution less saline than normal marine water or, subsequently, was flushed by a dilute solution that removed strontium but did not effect an inversion to stoichiometric dolomite.

The stoichiometric dolomite studied contains less strontium than the non-stoichiometric dolomite. This suggests protracted exposure to a less saline solution, allowing the stoichiometric dolomite to crystallize slowly in approximate equilibrium with the solution.

Folk and Land (1975) felt that the salinity, as well as the Mg/Ca ratio of a solution, might control dolomitization. Because dolomite is a well-ordered structure, it must form relatively slowly. Although dolomite is favored thermodynamically in hypersaline solutions supersaturated for both calcite and dolomite, calcite can form more quickly, and it is the more abundant precipitate. As calcite precipitates, the Mg/Ca ratio of the solution increases until a poorly ordered dolomite begins to form. Dolomite is also the favored precipitate in mixtures containing as little as 3 percent seawater (Land, 1973), if they have Mg/Ca ratios as low as 1/1. These solutions are oversaturated in dolomite, and slow crystallization in equilibrium of the dolomitic phase can occur.

Table 2 lists mean concentrations of strontium from various analyses of dolomite and the interpreted origin of those dolomites. The strontium-content of the dolomite in some lithofacies of this study is well below that of subtidal dolomite believed to have crystallized in equilibrium with seawater (Behrens and Land, 1972). The crystals of dolomite are 30 to 80 μ in size and much larger than the 1 to 5 μ dolomite crystals reported from modern supratidal environments. These features imply that the dolomitization in most of the microfacies studied probably occurred after the sediments were buried and during their exposure to a dilute mixture of seawater and freshwater.

Crystals of dolomite with hollow centers were observed in several lithofacies (pl. 2-B). Lippmann (1973, p. 167) hypothesized that hollow stoichiometric crystals of dolomite once may have had less-stable cores of calcian dolomite which later dissolved preferentially. Although Land, Salem, and Morrow (1975, p. 1604) suggested that hollow crystals of dolomite may imply two mechanisms or environments of dolomitization, penecontemporaneous dolomitization need not be invoked as an explanation for this phenomenon. Crystallization from a relatively saline, brackish solution could produce non-stoichiometric crystals of dolomite. A drop in the salinity of the dolomitizing fluid would allow for the slow crystallization of stoichiometric dolomite on the margins of the previously formed calcian crystals. A further decrease in salinity would result in the dedolomitization and dissolution of the less stable cores of calcian dolomite (Folk and Siedlecka, 1974). A drop in water-level in the groundwater-system of Hanshaw, Back, and Deike (1971) or seaward migration of the saltwater-freshwater interface (Land, Salem, and Morrow, 1975) could produce such a progressive salinity decrease.

SUMMARY

The carbonate sequences studied herein represent multiple transgressive-regressive cycles of sedimentation. Original textures are pre-

TABLE 1

Range and mean for the mol-percent $MgCO_3$ and strontium content groups (26 samples)

	Mol-percent $MgCO_3$		Strontium content (ppm)	
Group	low	high	low	high
Range	44-48	49-51	75-122	162-255
Mean	45	51	88	190

served more frequently in rocks deposited in a supratidal environment and totally replaced by stoichiometric dolomite. Non-stoichiometric dolomite is encountered more often with obscured or obliterated limestone-fabrics. Strontium in both stoichiometric and non-stoichiometric dolomite generally is less than 250 ppm and indicates formation in a solution less saline than seawater.

Some supratidal rocks may have been at least partly dolomitized penecontemporaneously with sedimentation. This relatively more rapid crystallization of finely crystalline dolomite permitted some preservation of texture, as it does in modern environments. Dolomitization continued with time as these rocks, and those of other depositional environments in the area, were buried and subjected to repeated lateral migration of a saltwater-freshwater interface and phreatic groundwater-conditions.

Stoichiometric dolomite and low values of strontium suggest near-equilibric conditions in which the rocks were in contact with dolomitizing fluid over a relatively long span of time. A slow rate of replacement facilitated textural preservation.

These interpretations are in agreement with the mechanisms hypothesized by Hanshaw, Back, and Deike (1971) and Land, Salem, and Morrow (1975). Mixing of near-surface, phreatic-meteoric water with deeper saline water or the migration of a saltwater-freshwater interface ("schizohaline" zone) can account for the dolomitization of a large volume of carbonate rock in the area. The final dolomitizing fluids were diluted mixtures of saline and fresher water.

ACKNOWLEDGMENTS

We are deeply grateful for the many suggestions, interpretations, points of guidance, and cooperation provided by William H. Morgan, Frank N. Blanchard, and Paul A. Mueller of the University of Florida, William Back of the U.S. Geological Survey, and Charles W. Hendry, Jr. of the Florida Bureau of Geology. This work was supported in part by

TABLE 2
Mean strontium concentrations from various dolomite analyses published and from this study

Description and reference	Strontium (ppm)
Subtidal dolomite, Holocene, Texas (Behrens and Land, 1972)	916
Dolomite from meteoric water, Pleistocene, Jamaica (Land, 1973)	220
Dolomite from meteoric water, Eocene, Egypt (Land, Salem, and Morrow, 1975)	90
Dolomite from meteoric water, Ordovician, Canada (Land, Salem, and Morrow, 1975)	81
Stoichiometric dolomite, Eocene, Florida (this study)	88
Non-stoichiometric dolomite, Eocene, Florida (this study)	190

funds provided by the U.S. Department of the Interior, Office of Water Research and Technology as authorized under the Water Resources Research Act of 1964 as amended.

REFERENCES

Al-Hashimi, W. S., 1976, Significance of strontium in some carbonate rocks in the Carboniferous of Northumberland, England: Jour. Sed. Petrology, v. 46, p. 369-376.

Behrens, E. W., and Land, L. S., 1972, Subtidal Holocene dolomite, Baffin Bay, Texas: Jour. Sed. Petrology, v. 42, p. 155-161.

Dunham, R. J., 1962, Classification of carbonate rocks according to depositional texture: Am. Assoc. Petroleum Geologists Mem. 1, p. 108-121.

Folk, R., and Land, L. S., 1975, Mg/Ca ratio and salinity: two controls over crystallization of dolomite: Am. Assoc. Petroleum Geologists Bull., v. 59, p. 60-68.

Folk, R. L., Roberts, H. H., and Moore, C. H., 1973, Black phytokarst from Hell, Cayman Islands, British West Indies: Geol. Soc. America Bull., v. 84, p. 2351-2360.

Folk, R. L., and Siedlecka, A., 1974, The "schizohaline" environment: its sedimentary and diagenetic fabrics as exemplified by Late Paleozoic rocks of Bear Island, Svalbard: Sedimentary Geology, v. 11, p. 1-15.

Goldsmith, J. R., and Graf, D. L., 1958a, Structural and compositional variations in some natural dolomites: Jour. Geology, v. 66, p. 678-693.

————1958b, Relation between lattice constants and composition of the Ca–Mg carbonates: Am. Mineralogist, v. 43, p. 84-101.

Hanshaw, B. B., Back, W., and Deike, R. G., 1971, A geochemical hypothesis for dolomitization by groundwater: Econ. Geology, v. 66, p. 710-724.

Hickey, E. W., ms, 1976, Sedimentology and dolomitization in Eocene carbonate rocks, Gilchrist and Marion Counties, Florida: M.S. thesis, Univ. Florida, 74 p.

Illing, L. V., Wells, A. J., and Taylor, J. C. M., 1965, Penecontemporaneous dolomite in the Persian Gulf: Soc. Econ. Paleontologists Mineralogists Spec. Pub. 13, p. 89-111.

Kinsman, D. J. J., 1969a, Interpretation of Sr^{+2} concentration in carbonate minerals and rocks: Jour. Sed. Petrology, v. 39, p. 486-508.

———— Modes of formation, sedimentary associations, and diagnostic features of shallow-water and supratidal evaporites: Am. Assoc. Petroleum Geologists Bull., v. 53, p. 830-840.

Land, L. S., 1973, Contemporaneous dolomitization of Middle Pleistocene reefs by meteoric water, North Jamaica: Bull. Marine Sci., v. 23, p. 64-92.

Land, L. S., Salem, M. R. I., and Morrow, D. W., 1975, Paleohydrology of ancient dolomites: geochemical evidence: Am. Assoc. Petroleum Geologists Bull., v. 59, p. 1602-1625.

Lippmann, F., 1973, Sedimentary carbonate minerals: New York, Springer-Verlag, 228 p.

Randazzo, A. F., and Saroop, H. C., 1976, Sedimentology and paleoecology of Middle and Upper Eocene carbonate shoreline sequences, Crystal River, Florida, U.S.A.: Sedimentary Geology, v. 15, p. 259-291.

Randazzo, A. F., Stone, G. C., and Saroop, H. C., 1977, Diagenesis of Middle and Upper Eocene carbonate shoreline sequences, central Florida: Am. Assoc. Petroleum Geologists Bull., v. 61, p. 492-503.

Shinn, E. A., Ginsburg, R. N., and Lloyd, R. M., 1965, Recent supratidal dolomite from Andros Island, Bahamas: Soc. Econ. Paleontologists Mineralogists, Spec. Pub. 13, p. 112-123.

Summerson, C. H., 1966, Crystal molds in dolomite: their origin and environmental interpretation: Jour. Sed. Petrology, v. 36, p. 221-224.

Veizer, J., and Demović, R., 1974, Strontium as a tool in facies analysis: Jour. Sed. Petrology, v. 44, p. 93-115.